

Electron transfer in non-oxovanadium(IV) and (V) complexes: Kinetic studies of an amavadin model*

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Abstract: Electron-transfer reactions of the eight-coordinate vanadium complex, bis-(*N*-hydroxyiminodiacetate)vanadium(IV) [V(HIDA)₂]²⁻, a synthetic analog of amavadin with ascorbic acid and hexachloroiridate(IV), have been studied. The self-exchange rate constant for this analog has been calculated from oxidation and reduction cross-reactions using Marcus theory and directly measured using ⁵¹V NMR paramagnetic line-broadening techniques. The average self-exchange rate constant for the bis-HIDA vanadium(IV/V) couple equals $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The observed rate enhancements are proposed to be due to the small structural differences between the oxidized and reduced forms of the HIDA complex and inner-sphere reorganizational energies. The electron-transfer reaction of this synthetic analog is experimentally indistinguishable from amavadin itself, although significant differences exist in the reduction potential of these compounds. This suggests that ligand modification effects the thermodynamic driving force and not the self-exchange process.

Keywords: vanadium; electron transfer; kinetics; amavadin; non-oxo; model complexes.

INTRODUCTION

Amavadin has been found in the mushroom *Amanita muscaria* where vanadium concentrations exceed 400 times those normally found in plants [1–6]. It was first reported in 1972 by Kneifel and Bayer [7,8] and later shown by Meisch and coworkers [9] that only one species of the more than 200 in the genus *Amanita* contained elevated vanadium concentrations. Although it was isolated over 30 years ago, the function of amavadin remains unknown. Many roles have been proposed, which include a redox mediator or an oxygen carrier. It has reversible redox chemistry with a one-electron reduction potential (+0.03 V in dimethylsulfoxide (DMSO) and +0.53 V in H₂O, both vs. SCE) [10].

Amavadin possesses an unusual non-oxovanadium(IV) center within an eight-coordinate environment formed through the 1:2 complexation of the vanadium metal with the natural (**1**) (not shown) or

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synthetic ligands (2) Fig. 1 [11–15], such as the tetradentate ligand (*S,S*)-2,2'-(hydroxyimino)dipropionic acid (HIDPA) [11]. Numerous spectroscopic [16] and crystallographic [13,15] studies have shown that the overall geometry is the same in both the reduced and oxidized states. Garner et al. have also synthesized HIDPA complexes coordinated to a number of other metals [17,18].

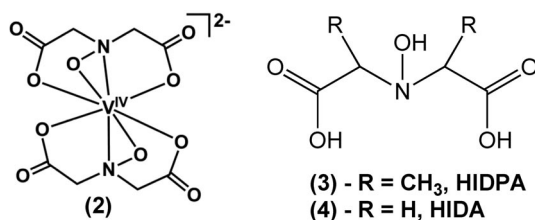


Fig. 1 Idealized structure of the synthetic amavadin analog, $[V(HIDPA)_2]^{2-}$ (2), left, and the natural ligand for amavadin (3) and the analog, right.

While the natural product $[V(HIDPA)_2]^{2-}$ (1), has been synthesized both in its racemic [11] and enantiomeric forms [20], the ligand synthesis is nontrivial. A simple analog to HIDPA, *N*-hydroxyiminodiacetate (HIDA) is much more synthetically accessible and possesses only one structural isomer in the vanadium complex [13,19]. The only significant structural difference between $[V(HIDPA)_2]^{2-}$ (2) and the natural product, $[V(HIDPA)_2]^{2-}$ (1), is the replacement of the methyl group on the ligand arms (3) with a hydrogen (4) as shown in Fig. 1. As a result of its ease of synthesis, the bis-HIDA vanadium complex (2) has been used in many studies probing the structure, electrochemistry, and reactivity of these non-oxo complexes [10,13,21–25].

We have recently determined an internally consistent self-exchange electron-transfer rate constant of the $[V(HIDPA)_2]^{2-/-}$ couple using both Marcus calculations as well as direct measurement by ^{51}V NMR line-broadening techniques [26]. Here we describe the determination of the self-exchange electron-transfer rate constant of the $[V(HIDA)_2]^{2-/-}$ couple using the same two techniques. This was undertaken to examine the effect of the changing ligand on the self-exchange rate of the model complex. The self-exchange rate is compared to that reported by Macartney for the $[VO(OH)_3]^{0/-}$ system where $k_{\text{et}} = 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [27], and our results with the parent naturally occurring amavadin reported previously where $k_{\text{et}} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [26].

EXPERIMENTAL

Materials

Potassium hexachloroiridate(IV) was obtained from Aldrich Chemical in 99.9 % purity and used without further purification since two different lots of this compound gave identical kinetic results. L-ascorbic acid (Eastman), ceric ammonium sulfate dihydrate (Allied), ceric ammonium nitrate (GFS), and anhydrous LiCl (Sigma-Aldrich) were used as purchased. Solution ionic strengths were kept at 1.0 M with solutions of HCl/LiCl, and all mixtures were prepared with either doubly distilled, nanopure H_2O or D_2O in the case of NMR studies. $\text{Ca}[V(HIDA)_2]$ was synthesized using slightly modified literature methods [15].

Stoichiometry and kinetic measurements

Reaction stoichiometries were determined spectrophotometrically using a Hewlett Packard HP8452A diode array spectrophotometer. Job plots were constructed from absorbance data for either formation or loss of $[\text{V}(\text{HIDA})_2]^-$ (506 nm) or for the disappearance of the oxidant, 490 nm for K_2IrCl_6 .

Kinetic studies were carried out at the aforementioned wavelengths using a D110 Durrum stopped-flow spectrophotometer interfaced with an OLIS data acquisition setup [28]. The temperature was held constant using a temperature bath. Initial ascorbate reduction studies used pseudo-first-order conditions with excess reductant. Subsequent studies used mixed second-order conditions for the ascorbate reduction. The V(V) oxidation state was formed in situ using stoichiometric amounts of Ce(IV). Mixed second-order conditions for the hexachloroiridate(IV) oxidation studies were used since the reaction rates were outside the stopped-flow range under pseudo-first-order conditions. In all cases, absorbance vs. time data were collected and fitted to more than three half lives. Pseudo-first-order conditions were used with the L-ascorbic acid in at least 10-fold excess (a concentration range from 5.0×10^{-4} – 0.10 M) over the V(V) concentration (5.0×10^{-5} M). Details of the second-order conditions used for the oxidation and reduction studies can be found in the Supplementary Information section. Each rate constant represents the average of three to five trials. OLIS Kinfit routines were used for pseudo-first-order conditions and with a typical error of no more than 10 %. Data fitting under mixed second-order conditions used Origin[®] fitting routines.

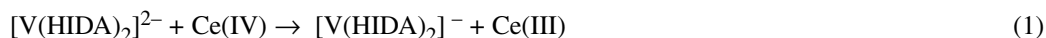
NMR spectroscopic measurements

^{51}V NMR measurements were carried out on a Varian 300 MHz NMR spectrometer at 79 MHz with VOCl_3 as the external reference. The internal temperature of the probe was kept constant at 25.0 ± 0.1 °C. In situ production of the diamagnetic V(V) species was undertaken using stoichiometry amounts of Ce(IV) to oxidize the V(IV) with the remaining V(IV) as the source of the paramagnetic species. This approach was necessary since it was found that the aqueous V(V) complex began to significantly decompose after a 30-min time frame so that a “stock” V(V) solution could not be used for these experiments. Data fitting of the observed line broadening used Origin-fitting routines.

RESULTS

Reaction stoichiometries

Ce(IV) has been used to produce V(V) complexes of amavadin and its analogs, and a stoichiometric study was recently reported with the parent complex [26] but no information is available for the model complex. Since the hydroxylamine part of the ligand could undergo oxidation, we have carried out studies with one-electron oxidants to confirm the expected stoichiometries. Absorbance changes vs. oxidant (or reductant) ratios were plotted as a function of oxidant/reductant mole ratios. When Ce(IV) was used to oxidize $[\text{V}(\text{HIDA})_2]^{2-}$ to $[\text{V}(\text{HIDA})_2]^-$, an equivalence point of 1.15 (Ce^{IV}):1.00 (V^{IV}) was observed. Subsequent to Ce(IV) oxidation, the reduction of $[\text{V}(\text{HIDA})_2]^-$ by ascorbic acid gave a stoichiometry of 0.99 (H_2Asc):2.00 (V^{V}). Oxidation by IrCl_6^{2-} showed an average equivalence point at 0.96 (Ir^{V}):1.00 (V^{IV}). Each Job plot (data not shown) showed sharp breaks in absorbance at the expected oxidant/reductant ratios, which indicates that the reactions studied go to completion. The following reactions can be written based on these results:



Ascorbic acid reduction kinetics

The reduction of $[\text{V}(\text{HIDA})_2]^-$ by ascorbic acid was studied under both pseudo-first-order and mixed second-order conditions. The latter method was required to study the acid dependence of this reaction since the reaction became too fast at higher pH to study under pseudo-first-order conditions.

Pseudo-first-order data

Ascorbic acid (H_2Asc) concentrations were in at least 10-fold excess over $\text{V}(\text{V})$ concentrations. Absorbance changes at 506 nm fit well to a single-exponential decrease to give observed first-order rate constants, k_{obs} . Plots of k_{obs} vs. ascorbic acid concentrations were linear with a zero y-intercept, and the slopes of the lines gave the observed second-order rate constants. This demonstrates a first-order dependence on both oxidant and reductant as shown in eq. 4.

$$-\text{d}[\text{V}(\text{HIDA})_2^-]/\text{d}t = k_{\text{asc}}[\text{H}_2\text{Asc}][\text{V}(\text{V})] \quad (4)$$

Second-order data

Above pH 1.0, mixed second-order conditions were used to determine the rate constants with ascorbic acid in a slight stoichiometric excess over $[\text{V}(\text{HIDA})_2^-]$. The agreement between this method and the pseudo-first-order approach was checked in a run at 0.10 M HCl. Using the 2:1 reaction stoichiometry, absorbance data was vs. time fit using a linearized form of eq. 5 [29,30].

$$-\ln \left(\frac{[\text{H}_2\text{Asc}]_0}{0.5[\text{V}(\text{HIDA})_2^-] + ([\text{H}_2\text{Asc}]_0) \left(\frac{A_o - A_\infty}{A_t - A_\infty} \right)} \right) = \left([\text{H}_2\text{Asc}]_0 - 0.5[\text{V}(\text{HIDA})_2^-] \right) k_{\text{asc}} t \quad (5)$$

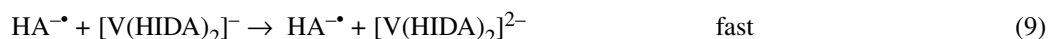
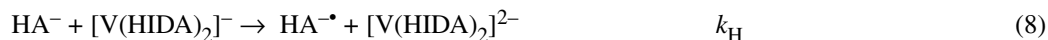
Reasonably good agreement was found between the second-order data and the pseudo-first-order data (560 and $400 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at pH 2.0). The details of this fit are similar to those for the $\text{Ir}(\text{IV})$ oxidation discussed below.

Hydrogen ion dependence

A plot of the second-order rate constants, k_{rxn} , obtained at each pH (from pseudo-first- and mixed second-order data) is linear for an inverse hydrogen ion concentration dependence and possesses a zero y-intercept, Fig. 2. Hydrogen ion concentrations varied between 0.10 and 0.25 M.

$$k_{\text{asc}} = k_a[\text{H}^+]^{-1} \quad (6)$$

The inverse dependence implies that only a single deprotonated species undergoes reaction. Since $[\text{V}(\text{HIDA})_2^-]$ does not have a dissociable proton, the logical source for dependence is the deprotonation of ascorbic acid.



An expression for k_a derived from the above scheme can be written as shown in eq. 10.

$$k_a = \frac{k_{\text{H}} K_{\text{a}}}{K_{\text{a}} + [\text{H}^+]} \quad (10)$$

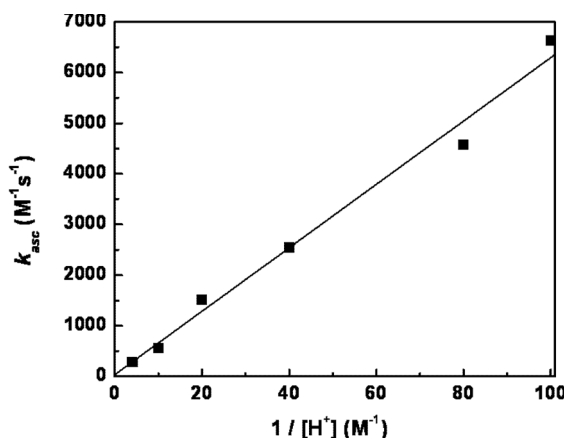


Fig. 2 Hydrogen ion dependence of the ascorbic acid reduction. The solid line is a linear fit of the data and corresponds to k_a in eq. 6. Conditions: $T = 25.0\text{ }^\circ\text{C}$, $I = 1.0\text{ M}$ (LiCl).

This relationship reduces to $k_a = k_H K_a [H^+]^{-1}$ in the limit where $[H^+] \gg K_a$, since the maximum pH in this study is 2.5. Therefore, using eq. 6, a value for k_H can be calculated to equal $(9.3 \pm 0.7) \times 10^5\text{ M}^{-1}\text{ s}^{-1}$ using the pK_{a1} for ascorbic acid equal to 4.17 [31].

Potassium hexachloroiridate oxidation kinetics

The hexachloroiridate(IV) oxidation of $[V(\text{HIDA})_2]^{2-}$ is expected to proceed via an outer-sphere mechanism. Assuming this, a simple rate law may be written for this process.

$$d[V(\text{HIDA})_2^-]/dt = k_{\text{Ir}}[\text{IrCl}_6^{2-}][V(\text{HIDA})_2^{2-}] \quad (11)$$

Unfortunately, the reaction was too fast to study under pseudo-first-order conditions so mixed second-order conditions were used to determine the electron-transfer rate constants. The absorbance vs. time data were fit over three half lives using eq. 12 [29] as shown in Fig. 3. This supports the rate law written in eq. 11.

$$\ln \left(\frac{[V(\text{HIDA})_2^{2-}]_0}{[K_2\text{IrCl}_6]_0 + ([V(\text{HIDA})_2^{2-}]_0 - [K_2\text{IrCl}_6]_0) \left(\frac{A_0 - A_\infty}{A_t - A_\infty} \right)} \right) = ([V(\text{HIDA})]_0 - [K_2\text{IrCl}_6]_0) k_{\text{Ir}} t \quad (12)$$

where the slope equals $\{[V(\text{HIDA})_2^{2-}]_0 - [K_2\text{IrCl}_6]_0\} k_{\text{Ir}}$. The experimental values for these constants can be found in the Supplementary Information.

As expected, the observed second-order rate constants, k_{Ir} , were invariant between pH 1.0 and 2.9, (1.9×10^6 and $1.5 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$, respectively) since neither reactant has an ionizable hydrogen over this pH range. The average rate constant for all experiments was determined to equal $(1.9 \pm 0.2) \times 10^6\text{ M}^{-1}\text{ s}^{-1}$. The temperature dependence of this reaction was studied and rate constants at five different temperatures were obtained, see the Supplementary Information. Using transition-state theory [29], the ΔH^\ddagger and ΔS^\ddagger of activation were calculated to equal $16 \pm 2\text{ kJ/mol}$ and $-24 \pm 3\text{ J/mol K}$, respectively. These values are small and consistent with a facile outer-sphere electron-transfer process [32].

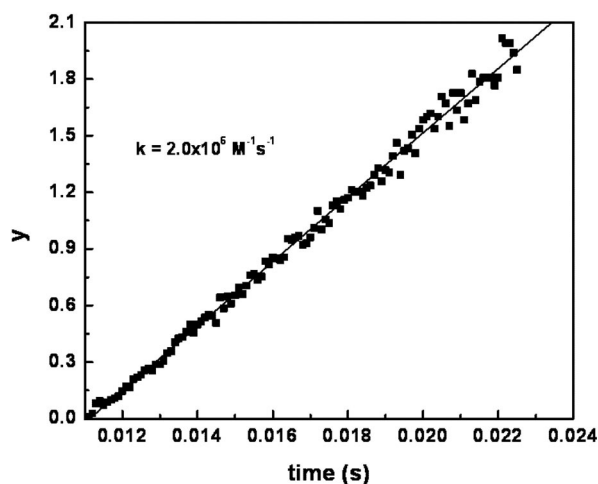


Fig. 3 Typical fitted second-order kinetic data for hexachloroiridate(IV) oxidation of $[\text{V}(\text{HIDA})_2]^{2-}$. The left side of eq. 12 was used to calculate the “y” value and the slope equals $([\text{V}(\text{HIDA})_2]_0 - [\text{IrCl}_6^{2-}]_0)k_{\text{Ir}}$. Conditions: $[\text{V}(\text{IV})] = 110 \text{ mM}$, $[\text{Ir}(\text{IV})] = 25 \text{ mM}$, $[\text{HCl}] = 0.10 \text{ mM}$, $[\text{LiCl}] = 0.90 \text{ mM}$, $T = 25.0 \text{ }^\circ\text{C}$.

Marcus calculations

Ascorbate and hexachloroiridate(IV) have been previously used as outer-sphere reagents and have well-established self-exchange rate constants [26,27], see Table 1. Marcus theory has been successfully applied to these reactants. In contrast, the application of Marcus theory to calculate self-exchange rate constants for the V(IV/V) couple is typically impossible since going from the +4 to the +5 oxidation state usually involves major structural changes, generally changes in oxo groups [5,6]. However, the non-oxo amavadin-like complexes [1–6] are ideal candidates for Marcus treatment since the overall coordination environment between the two oxidation states does not change. In addition, since there is no open coordination site in the $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple, both electron-transfer reactions will most likely occur via outer-sphere pathways. Because all the reactants in this study are negatively charged, a simplified (no work terms) Marcus approach was used to calculate the self-exchange rate constant for the $[\text{V}(\text{HIDPA})_2]^{-/2-}$ couple [26]. The relevant equations are

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (13)$$

$$\text{where } f_{12} = (\ln K_{12})^2 / 4[\ln(k_{11}k_{22}/Z^2)] \quad (14)$$

and K_{12} can be calculated using the standard reduction potentials (vs. SHE) listed in Table 1. The collision frequency, Z , was set to equal $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Using the self-exchange constants, k_{11} , listed in Table 1, a value for k_{22} was calculated for the self-exchange for the $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple. The values for the ascorbate reduction and hexachloroiridate(IV) oxidation are $1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $5.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Although the agreement between these two values is limited, it is as good as expected for such simple calculations. An average value of $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated for the self-exchange rate constant for $[\text{V}(\text{HIDA})_2]^{-/2-}$.

Table 1 Marcus cross-relationship data.

$[\text{V}(\text{HIDA})_2]^{-/2-}$ ($E^\circ = 0.87 \text{ V vs. SHE}$)							
Reagent	$E^\circ \text{ (V)}$	$\Delta E \text{ (V)}$	k_{11}	k_{12}	K_{12}	f_{12}	k_{22}
L-Ascorbate	0.70	0.17	1.00×10^5	9.3×10^5	751	0.689	1.7×10^4
K_2IrCl_6	0.96	0.09	2.30×10^5	1.9×10^6	33.3	0.885	5.3×10^5

⁵¹V NMR line broadening

The rate constants for outer-sphere electron transfer between anions have been measured using NMR paramagnetic line-broadening experiments as described previously [26]. When electron transfer between diamagnetic and paramagnetic ions occurs in the “slow-exchange” region on the NMR time scale, a direct measurement of the self-exchange rate constants can be made using eq. 15.

$$k_{22}[\text{V(HIDA)}_2]^{2-} = \pi(W_{\text{DP}} - W_{\text{D}}) \quad (15)$$

W_{DP} and W_{D} are the line widths at half height for the observed resonances in the presence and absence of the paramagnetic ion, and k_{22} is the self-exchange rate constant. The line widths were measured from the spectra processing using no line broadening and by fitting the data using Origin 7.

In order to confirm the values calculated using Marcus theory in the previous section, experiments were carried out to measure the paramagnetic line broadening induced by addition of known amounts of $[\text{V(HIDA)}_2]^{2-}$ of the ^{51}V signal for $[\text{V(HIDA)}_2]^-$. Figure 4 shows a typical plot of line width (W_{DP}) at half height vs. $[\text{V(HIDA)}_2]^{2-}$. The slope of this line equals k_{22}/π , and the intercept equals W_{D} . An average rate constant equal to $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was calculated from all experiments and is in excellent agreement with the average value calculated from the Marcus cross-relationship in the previous section.

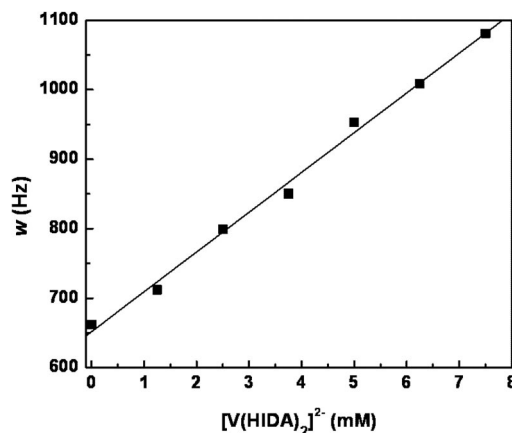


Fig. 4 A typical plot of the paramagnetic line broadening [W_{DP} (Hz)] as a function of the paramagnetic V(IV) concentration; the ^{51}V NMR spectra were recorded at $0.050 \text{ mol dm}^{-3}$ $[\text{V(HIDA)}_2]^-$ using VOCl_3 as a reference. Conditions: $T = 25.0^\circ\text{C}$, $I = 1.0 \text{ M}$ (LiCl), $[\text{HCl}] = 0.10 \text{ M}$. The line is a linear fit of the data, $k_{\text{et}} = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Only three other determinations of self-exchange rate constants for V(IV/V) complexes have been reported [26,27,34]. Macartney et al. used the Marcus cross-relationship to calculate a self-exchange rate constant for the $[\text{VO(OH)}_3]^{0/-}$ couple equal to $\sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [27]. This is significantly slower than that reported for our value for the natural product, amavadinine $[\text{V(HIDPA)}_2]^{-/2-}$ [26]. Since only small structural differences are observed in the oxidized and reduced forms of the natural product, the inner-sphere reorganizational energy must be smaller than that of the “aqueous” vanadium couple described by Macartney. This decrease in the activation barrier would result in an increase in the self-exchange rate constant.

One other V(IV/V) exchange rate constant was first reported by Giuliano and McConnell [33] and later re-examined by Okamoto et al. [34]. Both studies used ^{51}V NMR paramagnetic line broadening when $\text{VO}^{2+}(\text{aq})$ was added to solutions of $\text{VO}_2^+(\text{aq})$. The rate law established by both groups was first order with respect to $[\text{VO}_2^+]$ and second order with respect to $[\text{VO}^{2+}]$. The second-order term in V(V)

arises from complex formation between V(IV) and V(V) followed by electron transfer between the adduct and monomeric V(V). Okamoto et al. determined this electron-transfer rate constant to equal $1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 5.4 M HClO_4 (and presumably 25 °C) [33]. They attributed their higher rate constant, compared to Macartney's [27], to result from smaller activation barriers due to similarities in V–O bond lengths in the dimer and $\text{VO}_2^+(\text{aq})$. This description is analogous to our analysis for the high self-exchange rate constant for $[\text{V}(\text{HIDA})_2]^{-/2-}$, i.e., decreased inner-sphere reorganization terms. The V–O equatorial and V–O axial bond lengths only decrease by $0.12 (\pm 0.03)$ and $0.005 (\pm 0.008) \text{ \AA}$, respectively, while the V–N bond lengths increase by $0.020 (\pm 0.009) \text{ \AA}$ [22].

CONCLUSION

The oxidation and reduction reactions for the title complexes proceed via outer-sphere electron-transfer mechanisms. The measured rate constant for the $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple is 2–3 orders of magnitude larger than for $[\text{VO}(\text{OH})_3]^{0/-}$, which was a calculated value using Marcus theory [27]. The larger value for the $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple is most likely due to lower inner-sphere reorganization energies since the oxidized and reduced species have small differences in their metal-to-ligand bond distances. The observed self-exchange rate constant for $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple ($1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), is indistinguishable from the self-exchange rate constant observed for the natural product amavadin, $[\text{V}(\text{HIDPA})_2]^{-/2-}$ ($1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). Any structural rearrangement required to convert between V(IV) and (V) represents fine-tuning that may take place is not sufficiently large to translate into a measurable difference in the exchange-rate constant.

The non-oxo $[\text{V}(\text{HIDA})_2]^{-/2-}$ couple now joins $[\text{V}(\text{HIDPA})_2]^{-/2-}$ as an example of the measured self-exchange rate constants for metals forming oxo metal complexes in aqueous media. These studies demonstrate that it is acceptable to use the amavadin model complex, $[\text{V}(\text{HIDA})_2]^{-/2-}$, in place of the less accessible natural product in reactivity studies and synthetic applications. Any reactivity of the model system can be attributed to the increased redox potential and not the self-exchange rate constant.

SUPPLEMENTARY INFORMATION

Further details are available online (doi:10.1351/PAC-CON-08-08-23).

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